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CHROMATOGRAPHIC AND MASS SPECTROMETRIC TECHNIQUES FOR THE DETERMINATION OF CHEMICALS OF EMERGING CONCERN

S. Krishna Kumar, Nikhil Patil and R. Babu Rajendran
Department of Environmental Biotechnology
School of Environmental Sciences
Bharathidasan University
Tiruchirappalli-620024, INDIA
Email: ramaswamybr@gmail.com

1. Introduction

Recent advancements in instrumentation has resulted in significant progress in trace level detection of Chemicals of Emerging Concern (CECs) in environmental matrices. The CECs do not necessarily mean new substances and they comprise a broad category of compounds, which are earlier unfamiliar or unrecognized for their potential toxicity in humans as well as in environment. Often these CECs are recognised as potential endocrine disruptors. They include brominated and organophosphate flame retardants, plasticizers, perfluorinated compounds (PFCs), surfactants, natural and synthetic hormones, pharmaceuticals and personal-care products (PPCPs), drugs of abuse and their metabolites, disinfection by-products, organometallics, nanomaterials, pesticides degradation/transformation products, algal and cyanobacterial toxins (Wille et al., 2012).

Due to the potential hazard of CECs, awareness on their monitoring in environmental matrices is increasing in 21st century. Often the choice of technique for analysing CECs is of either the Gas Chromatography (GC) or Liquid Chromatography (LC). Among them, GC-MS is used to identify and quantify volatile and semi-volatile compounds whereas LC techniques used to determine polar and less volatile compounds. Specifically GC-MS is used when resolution is crucial to separate isomers or congeners (Pietrogrande & Basaglia, 2007).

The performance of the instrument is ranked based on their limit of detection (LOD). As observed, LOD of coupled mass spectrometry techniques are lower (higher sensitivity) than LOD of other conventional instruments using detectors like UV, FID, ECD, etc. General procedure for the analysis of CECs in aqueous matrices is given in fig. 1.

2. Extraction Techniques

Sample preparation is one of the most critical steps next to sampling. Among the available techniques, liquid-liquid extraction (LLE) has been widely used as a pre-treatment technique for separation and preconcentration of organic analytes from aqueous samples until last decade. To overcome the limitations of LLE, recently popular solid phase extraction (SPE) was developed. Apart from these, miniaturized methodologies encompassing microextraction are being currently developed and used. The widely performed liquid phase

microextraction includes HF-LPME and DLLME, which mostly reduces the pre-concentration and cleanup procedures (Mahugo-Santana et al., 2011). Different types of liquid-phase microextraction techniques are mentioned in fig. 2. Direct and headspace solid phase microextraction (SPME) are also increasingly practiced in the analysis of environmental samples (Pietrogrande & Basaglia, 2007).

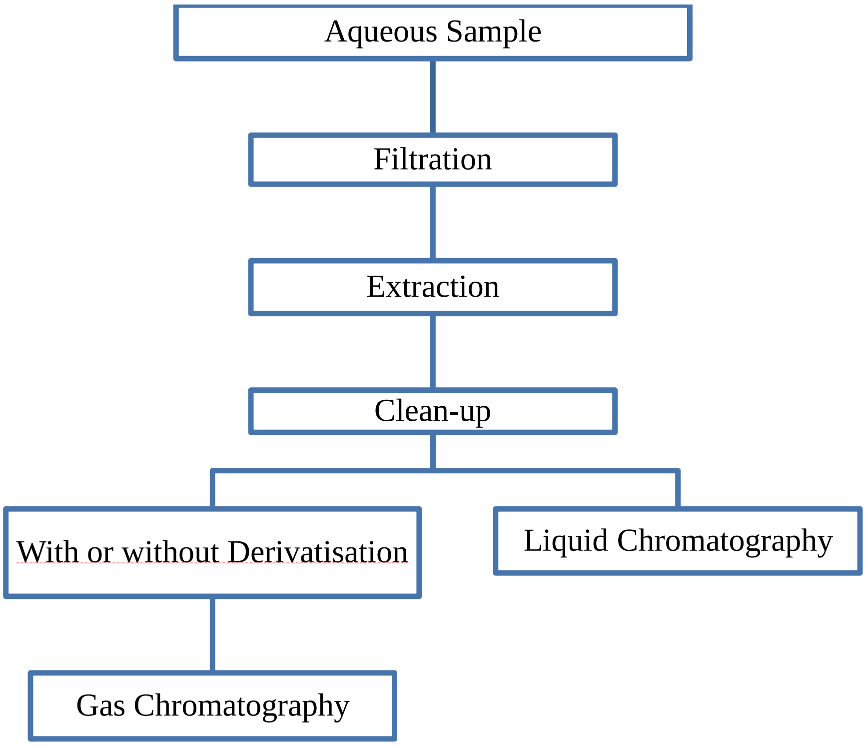

Fig 1 - General procedure for the analysis of CECs in aqueous matrices

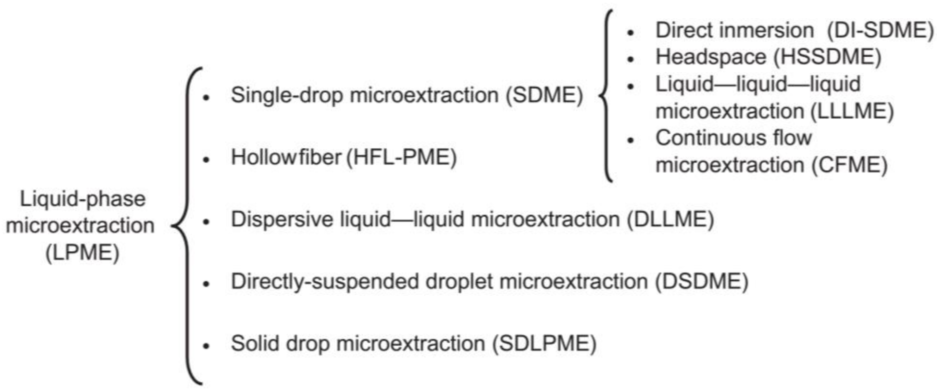

Fig 2 - Classification of liquid-phase microextraction techniques (Mahugo-Santana et al., 2011)

3. Pharmaceuticals

Pharmaceuticals are biologically active at therapeutic doses and many of them like non-steroid anti-inflammatory drugs (NSAIDs) are readily available over the counter being non-prescription drugs. As mentioned above, recent methods for quantifying trace amounts of pharmaceuticals and personal care products in the environment are primarily based on the application of gas chromatography (GC) and high-performance liquid chromatography (HPLC) with detector being generally a mass spectrometer. Based on GC-MS ng level analytical precision (LOD of 0.16-0.31 ng/L) for NSAIDs (Diclofenac, ketoprofen, naproxen, ibuprofen, and acetylsalicylic acid) was achieved by using derivatising agent (N-Methyl-N-(trimethylsilyl) trifluoroacetamide [MSTFA]) with extraction method recovery of 70-120% (Shanmugam et al., 2014). Similarly, neuroactive compound, carbamazepine, was also successfully determined in GC-MS with MSTFA derivatisation in south Indian rivers and the LOD obtained was 1.6 ng/L (Ramaswamy et al., 2011).

The use of advanced LC-MS/MS in environmental analysis permitted comprehensive assessment of environmental contaminants (PPCPs, antibacterials, NSAIDs and hormones) with LODs less than 1 ng/L (Kot-Wasik et al., 2007). Additionally, a multiresidue method was reported for the analysis of 54 PPCPs in surface water and wastewater by ultra-performance liquid chromatography – tandem mass spectrometerr (UPLC-MS/MS) with moderate LOD (50-10,000 ng/L) (Kasprzyk-Hordern et al., 2008).

However, another multiresidue method developed to detect 50 pharmaceuticals (including 26 antibiotics) in watewater using UPLC-MS/MS showed quite lower instrumental LOD at pg level (0.1-8 pg) (Gracia-Lor et al., 2011).

4. Personal Care Products

Ingredients such as preservatives (parabens), antimicrobials (triclosan, triclocarbon), emulsifiers, fragrances (synthetic musks) are added in personal care products (PCPs) such as hair spray, soaps, perfumes, shampoos, air fresheners, and cosmetics, household detergents, etc. Among PCPs Peck et al. (2006) analysed synthetic musk fragrances (Celestolide and Galaxolide) in lake sediment cores using GC- MS with the detection limit ranging from 0.025 ng/g to 5.1 ng/g.

Furthermore, Mottaleb et al. (2009) reported multi determination method for analysing UV filters, synthetic musks, alkylphenols, antimicrobials, and insect repellent in fish based on GC–SIM–MS and GC–MS/MS methodologies with method detection limits (MDLs) ranging from 2.4 to 16 ng/g, and 5.1 to 397 ng/g, respectively (Mottaleb et al., 2009).

5. Plasticizers

Amidst the plasticizers, phthalate esters are well known for their environmental contamination and toxicological effects as “endocrine disruptors.” In riverine environment phthalates were reported in water and sediment of south Indian river (Kaveri) based on SPE and GC-MS analysis (Selvaraj et al., 2015). Further, the study mentioned LOD and LOQ of 0.47-1.22 ng/ml and 1.55-4.07 ng/ml with recovery ranging from 33-121%. In case of bisphenol A, LOQ was reported as 8.5 ng/g for LC-MS/MS method as part of multiresidue analysis of CECs (Berlioz-Barbier et al., 2014).

6. PFCs

The widely used chemical for protective coating in various manufactured goods (carpets, apparel, firefighting foams and paper) includes perfluorinated compounds (PFCs). Among the PFCs, perfluorooctane sulfonate (PFOS) has received worldwide attention for its potential toxicity and therefore proposed as a candidate for persistent organic pollutants (POPs) under the Stockholm Convention (Yeung et al., 2009). Zainuddin et al., 2012 investigated perfluorooctanoic acid (PFOA) and PFOS in surface water of Malaysia using LC-MS/MS with lower detection limit (0.01 ng/ml). In case of sediment samples, Corsolini et al. (2012) achieved comparatively higher LOD 0.5 ng/g to report PFCs in India rivers.

7. Conclusion

Based on the above-discussed techniques, it is understood that coupled chromatographic techniques are capable of performing CECs determination at ng level. Especially tandom mass spectrometric techniques facilitated us to reach LODs upto pg level. In addition to the instrument, development in extraction techniques was also responsible for achieving lower LODs in multiresidue analysis based on their uniqueness such as high recoveries, minimised interference, high enrichment factors and minimised solvent consumption. Therefore, with the present sufficient analytical procedure, researchers are generating numerous reports on CECs incidence in environment for further action such as ban/restriction of CECs for safeguarding human and environmental health.

Table 1 – Use of popular coupled gas chromatography-mass spectrometry technique in analysis of CECs along with analytical precision

Sr. No.	Matrix	Volume of Sample	CECs	Extraction Method	Derivatization	LOD	LOQ	Recovery %	Analytical Method	Reference
1	River Water	1 L	Bisphenol A	SPE	MSTFA	1.5 ng/L	5.1 ng/L	93.9	GC-MS	Selvaraj et al. (2014)
			Nonyl Phenol			0.3 ng/L	1.1 ng/L	74.1		
			Octyl Phenol			1.1 ng/L	3.5 ng/L	71.8		
2	River Water	1 L	Triclosan	LLE		3 ng/L		100	GC-MS	Ramaswamy et al. (2011)
			Cabamazepine	SPE	MSTFA	1.6 ng/L		102		
			Parabens	SPE	MSTFA	0.5-0.6 ng/L		81-98		
3	River Water	0.5 L	NSAIDs	SPE	MSTFA	0.16-0.31 ng/L		70-120	GC-MS	Shanmugam et al. (2014)
4	River Water	0.5 L	Phthalates	SPE		0.47-1.22 ng/mL	1.55-4.07 ng/mL	33-121	GC-MS	Selvaraj et al. (2015)
5	River Sediment	1 gm	Phthalates	Ultrasonication		0.47-1.22 ng/mL	1.55-4.07 ng/mL	79-108	GC-MS	Selvaraj et al. (2015)
6	River Sediment	10 gm	Triclosan	Mechanical Shaker		1.5 ng/L		85	GC-MS	Ramaswamy et al. (2011)
7	Breast Cancer Tissue	1 gm	Parabens	Mechanical Shaker	MSTFA	1.05-3.75 ng/g	3.49-12.5 ng/g	96-113	GC-MS	Shanmugam et al. (2010)

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